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(54) PROCESS FOR THE PRODUCTION OF POLYETHER ISOCYANATES

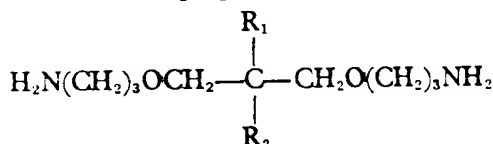
(71) We, WYANDOTTE CHEMICALS CORPORATION, a Corporation organized under the laws of the State of Michigan, United States of America, of 1609 Biddle Avenue, Wyandotte, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for the production of isocyanates.

The conversion of aliphatic amines by phosgenation to the corresponding isocyanates is known in the art. It is also known that diamines which contain ether groups upon phosgenation yield mainly ether cleavage products as can be seen in Siefken *Annalen der Chemie*, Volume 562, starting on page 75 (1949). This article reports an extensive amount of work on ether-containing diamines and reports that by incompletely phosgenating the dihydrochloride of diaminodipropyl

ether suspended in toluene, the filtrate obtained by filtering off the unreacted dihydrochloride contains some diisocyanate. The article states that ether diamines which may be obtained by the addition of acrylonitrile to difunctional alcohols and subsequent hydrogenation, such as ethylene glycol diaminodipropyl ether, yield mainly cleavage products during phosgenation while the desired diisocyanates are obtained only in very poor yield (page 87). The fact that mainly cleavage products and poor yields are obtained is also supported by Lehmann et al U. S. Patent No. 3,267,122. Accordingly, the use of diamines containing ether groups in the production of diisocyanates has been considered to be commercially impractical.

The Lehmann et al patent overcomes this problem, generally speaking, by providing a process for the production of isocyanates which comprises reacting phosgene with an amine having the following formula:



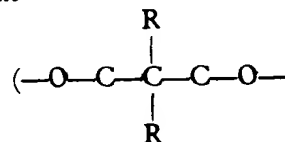
wherein R₁ and R₂ are selected from the group consisting of alkyl, aryl, cycloalkyl, haloalkyl, α -aminopropoxyalkyl and mixtures thereof. The term "cycloalkyl" includes, among others, two cycloalkyl radicals which form a closed cycloaliphatic ring.

The process of this patent has certain inherent disadvantages due to the necessity of using an amine having the above general formula which the patent indicates as essential by the statement:

"Only when using certain amines (as above defined in the formula) will the corresponding isocyanate be formed in desirable yields."

The necessity for using amines having the formula set forth above has certain inherent limitations, including by way of example:

1. The highly specific structural requirement

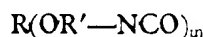


of a β -blocked diether severely limits the applicability of the disclosed invention.

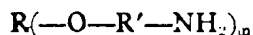
2. The required β -blocked diols are not readily available and are obtainable only through cumbersome and difficult syntheses.
3. The phosgenation procedure employed requires the additional step and added cost of converting the amine to hydrochloride of carbamate prior to introduction of the phosgene.

Accordingly, there is a need for a method for the production of polyether polyisocyanates without the disadvantages of production of ether cleavage products, or of undesirable low yields and other disadvantages of the prior art. Furthermore, the production of polyether polyisocyanates has hitherto been effected by carrying out the reaction in suspension. We have found a method for carrying out a reaction in solution.

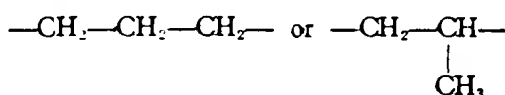
According to the invention there is provided a method of producing an isocyanate having the general formula



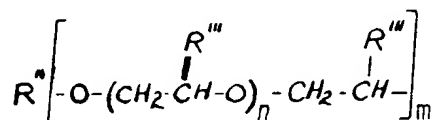
by reacting in solution, phosgene with an amine of the formula:



where m is 2 or 3, R' is



and R is an unbranched alkylene group having from 2 to 6 carbon atoms, or an oxyalkylene group having from 4 to 8 carbon atoms, or a cycloalkylene group (other than a 1,1-cycloalkylene group) having from 4 to 8 carbon atoms or a group having the general formula



wherein R'' is a di- or trifunctional alkylene group having from 2 to 6 carbon atoms, or an oxyalkylene group having from 4 to 8 carbon atoms, or an alkyl diarylene group having up to 25 carbon atoms, R''' is hydrogen or a lower alkyl group having 1 or 2 carbon atoms i.e., methyl or ethyl, m is 2 or 3 and n is an integer of from 1 to 20.

In the performance of this process, it is preferred to react the polyether amine of the above formula with phosgene in an inert solvent by contacting the amine with phosgene at a temperature in the range of 0 to 60° C. for a period of 30 to 120 minutes and then

continuing the phosgene addition while the mixture is heated to and maintained at a temperature in the range of 100 to 175° C., preferably 125 to 150° C., until a clear solution is obtained. This generally requires 2 to 20 hours. The solvent is removed by distillation from the polyisocyanate.

The amines which are used as a reaction component in the present process can be prepared by any of the known methods. They can, for example, be prepared by the reaction of acrylonitrile with difunctional and trifunctional alcohols and subsequent hydrogenation of the resulting reaction mixture. Typical of the alcohols that may be used are 1,2-ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,2-butyleneglycol, diethylene glycol, polypropylene glycol having molecular weight from 500 to 2200, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 1,4-dihydroxymethylcyclohexane, and polyether triols derived by condensation of 1,1,1-trimethylolpropane and propylene oxide.

The phosgenation of the amines may be effected by known methods such as, for example, by cold phase-hot phase phosgenation and can be carried out intermittently or in a continuous manner. It is preferred for best results that an inert solvent be used in the process of this invention. Typical solvents are toluene, xylene, chlorobenzene, orthodichlorobenzene and nitrobenzene.

The polyisocyanates obtained are valuable intermediate products for the production of polyurethane elastomers and foams by the isocyanate polyaddition process. They can be used as such, and also for example, as urethane polyisocyanates by addition of polyalcohols to these isocyanates, one OH equivalent preferably being used for two NCO equivalents, and also as diisocyanates comprising urea groups by reaction of water with the isocyanate at lower or only slightly elevated temperatures. In addition, trimerization products of the isocyanates may be used as well as polyisocyanates comprising biuret groups, such as those obtainable according to French Patent No. 1,228,477 or as masked polyisocyanates which liberate their NCO groups in known manner under heat.

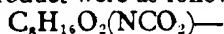
The preparation of polyurethanes from isocyanates is disclosed in many references including the texts entitled "Polyurethanes" by Bernard A. Dombrow, published by Reinhold Publishing Corporation, New York, New York, 1957, and "POLYURETHANES: Chemistry and Technology" by J. H. Saunders and K. C. Frisch, published by Interscience Publishers, New York—London, wherein disclosures are made of methods for producing polyurethanes.

The examples set forth below further illustrate the present invention.

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EXAMPLE 1

400 Grams of xylene was saturated at 25° C. with phosgene in a two-liter, round-bottomed flask fitted with a stirrer, additional funnel, thermometer, gas dispersion tube, and reflux condenser which in turn was connected to a gas absorption trap. A 6 weight percent solution of 1,2-ethylene-bis(1,3-oxypopylamine) in xylene (containing 18.9 g. of amine) was added from the addition funnel over a period of 43 minutes while simultaneously passing in phosgene through the dispersion tube. During the addition, a reaction temperature of 23 to 27° C. and a phosgene to amine molar feed ratio of 5:1 were maintained. When the amine addition was completed, the phosgene feed rate was reduced and the reaction mixture heated to and maintained at 130 to 135° C. until the mixture became clearer, which required 4 hours. The solvent was stripped off under vacuum and the crude product distilled to give 16.3 g. (63% of the theoretical) of 1,2-ethylene-bis(1,3-oxypopyl isocyanate) which distilled at 120° C. and 0.6 mm. Hg pressure. The residue from the distillation (polymeric isocyanates) correspond to 38 weight percent of the theoretical yield. No *v*-chloropropyl isocyanate (the expected product if cleavage occurred) was obtained in the distillation. The results obtained by elemental analysis of the product were as follows:



Calculated: C=52.62%; H=7.07%;
N=12.27%; NCO=36.8%.
Found: C=52.88%; H=7.26%;
N=12.32%; NCO=35.1%.

The percent NCO in this and subsequent examples was determined by A.S.T.M. Method D 1638—61T.

EXAMPLE 2

Using essentially the same method steps and conditions as in Example 1, and 8 weight percent solution of 2,3-butylene-bis(oxypopylamine) in xylene was phosgenated. A feed ratio of 6 moles of phosgene per amine equivalent was used and the reaction mixture became clear after 4 hours at reflux.

Distillation of the crude product at 121 to 126° C. and 0.7 mm. Hg pressure gave a 72% yield of distilled product which contained 32.1% NCO (32.7% NCO theoretical). As in Example 1, no cleavage products could be found during distillation. The results obtained by elemental analysis of the products were as follows:



Calculated: C=56.23%; H=7.87%;
N=10.93%.

Found: C=56.45%; H=8.05%;
N=11.10%.

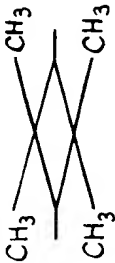
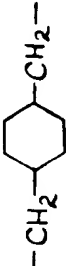



EXAMPLE 3

A polyethertri-amine of 174.5 neutral equivalent having a molecular weight of 523.5, prepared by the cyanoethylation and hydrogenation of a polyoxypopylene adduct of trimethylolpropane was phosgenated under the conditions given in Example 1. The amine feed solution was a 15 weight percent solution of amine in xylene, the phosgene-amine feed ratio was maintained at approximately 6 moles phosgene per amine equivalent, and the reaction mixture was heated at 130 to 135° C. for 5 hours. After stripping off the solvent, the crude product (quantitative weight yield) was heated for 3 hours at 150° C. and 4 mm. Hg pressure. The crude product was then passed through a molecular still (270 to 290° C., 15 to 25 μ pressure) to separate the product from polymeric residues. The distillate which was a clear, yellow mobile liquid amounted to a 71% yield and contained 20.8% NCO (theory=21.0% NCO).

EXAMPLES 4—13

To show the diverse applicability of this process, a series of aminopolyethers having the structural formulae, shown in Tables I and II below, were phosgenated under the conditions of Example 1. Where possible, the products were distilled or passed through a molecular still. The conditions and results with each of these preparations are given in Tables I and II below. To indicate the limited amount of cleavage which occurred, the percent fixed chlorine (total chlorine-hydrolyzable chlorine) is reported in Table I.

TABLE I

Example	Aminopolyether Used, $R-(OCH_2CH_2CH_2NH_2)_n$ wherein R is	Reaction Conditions			Product			
		Feed Conc., as % by wt. Amine in Xylene Solvent	Feed Ratio (1)	Yield, %	Boiling Range °C./mm. Hg Pressure	Weight % NCO, Theory	Weight % NCO, Found	% Fixed Chlorine
4		10	7.7	77	141/0.5-0.2	27.1	26.6	0.04
5		10	6.8	76	193/0.5-195/0.4	27.1	25.9	0.08
6		10	6.0	73	150-151/1.1	28.0	27.7	0.13
7	 (3)	26	6.5	77	(4)	14.2	14.0	0.16
8	 (5)	50	6.6	100	(2)	6.75	6.70	0.2

(1) Moles phosgene per equivalent of amine.

(2) Undistilled product.

(3) Prepared from approximately 400 molecular weight polyoxypropylene glycol. Neutral equivalent = 270.

(4) Product passed through a molecular still at 250-260°C./19-50 μ pressure.

(5) Prepared from approximately 1000 molecular weight polyoxypropylene glycol. Neutral equivalent = 595.

(4) Product passed through a molecular still at 250—260 °C./19—50 μ pressure.
 (5) Prepared from approximately 1000 molecular weight polyoxypropylene glycol. Neutral equivalent = 595.

TABLE II

Example	Aminopolyether Used, (Complete Formula)	Reaction Conditions			Product		
		Feed Conc., as % by wt. Amine in Xylene Solvent	Feed Ratio (1)	Yield %	Boiling Range °C./mm. Hg Pressure	Weight % NCO, Theory	Weight % NCO, Found
9	$\text{CH}_3-\text{CH}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ $\text{CH}_2-\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	6	3.5	66	116—120/0.6—0.8	34.7	33.2
10	$\text{O}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$	8	6.0	53	163—168/1.5—3.3	30.9	29.3
11	$\text{H}_2\text{N}(\text{CH}-\text{CH}_2\text{O})_n-\text{CH}_2\text{CH}-\text{NH}_2$ (4) CH_3	20	4.0	96	(3)	16.4	16.7
12	$\text{H}_2\text{N}(\text{CH}-\text{CH}_2\text{O})_m-\text{CH}_2\text{CH}-\text{NH}_2$ (4) CH_3	20	15	100	(2)	3.64	3.86
13	Diaminated, oxypropylated Bisphenol A Neutral Equivalent 348	30	6.3	67	(3)	11.2	10.4

(1) Moles phosgene per equivalent of amine.

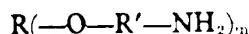
(2) Undistilled product.

(3) Product passed through a molecular still at 250—260 °C./19—50 μ pressure.

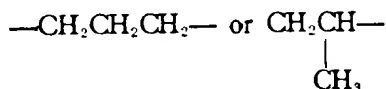
(4) Obtained by reaction of ammonia with polypropylene glycol. The amine in Example 11 has a neutral equivalent of 230.5 while that in Example 12 has a neutral equivalent of 1128.

WHAT WE CLAIM IS:—

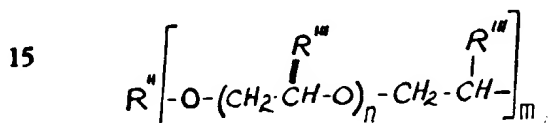
1. A method of producing an isocyanate having the general formula $R(OR'-NCO)_m$ by reacting, in solution, phosgene with an amine of the formula: :



in which m is 2 or 3, R' is



- 10 and R is an unbranched alkylene group having from 2 to 6 carbon atoms, or an oxyalkylene group having from 4 to 8 carbon atoms, or a cycloalkylene group (other than a 1,1-cycloalkylene group) having from 4 to 8 carbon atoms or a group having the general formula



wherein R'' is a di- or trifunctional alkylene group having from 2 to 6 carbon atoms, or

an oxyalkylene group having from 4 to 8 carbon atoms, or an alkyl diarylene group having up to 25 carbon atoms, R''' is hydrogen or methyl or ethyl, m is 2 or 3 and n is 1 to 20.

2. A method according to claim 1, in which said reaction is conducted in an inert solvent.

3. A method according to claim 1 or 2, in which the amine is contacted with phosgene at from 0 to 60° C. and thereafter the mixture is heated to and maintained at 100 to 175° C. until a clear solution is obtained.

4. A method according to claim 3, in which the amine is contacted with phosgene at 0 to 60° C. for from 30 to 120 minutes.

5. A method according to either of claims 3 and 4, in which the mixture is maintained at 100 to 175° C. for 2 to 20 hours.

6. A method according to any one of claims 1 to 5, of producing an isocyanate substantially as hereinbefore described in the Examples.

7. Isocyanates when produced by a method according to any one of claims 1 to 6.

STEVENS, HEWLETT & PERKINS,
Chartered Patent Agents,
5, Quality Court, Chancery Lane,
London, W.C.2.

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